

## STUDY OF INTERACTION BETWEEN COPPER AND MELT OF LEAD-FREE SOLDERS

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Preliminary Note – Prethodno priopćenje

Problems of reactive diffusion at the interface solid phase - melt were studied theoretically and experimentally. A theoretical description of the kinetics of dissolution of the solid phase in the melt is presented for the case of planar dissolution. The main intention was to study experimentally the copper dissolution in melts of various solder alloys and the related reactive diffusion. We used pure Sn and Sn-Cu, Sn-Ag-Cu, Sn-Sb, Sn-Zn alloys as solder materials. Experiments aimed at the study of a Cu plate dissolving in the solder melt were carried out at various conditions. Concentration profiles of elements and thickness of layers of phases were determined by SEM and X-ray microanalyses (WDX, EDX) of specimens after their heating.

**Key words:** lead-free solders, copper, tin, silver, intermetallic compounds, diffusion

### INTRODUCTION

This article deals with the problems of dissolution of the solid phase A in the melt B [1, 2]. Diffusion of atoms of the melt into the solid phase was accompanied by creation of new phases and/or chemical reactions, and finally by diffusion of atoms from the solid phase into the melt. Those processes usually proceed at the presence of convection in the melt. At the same time the process of significant movement of the interface between the solid phase and the melt takes place, the rate of which depends on the properties of atoms in A and B and on their interaction, temperature and time of the process in question. Furthermore, it depends on the geometric arrangement, on the volume of the melt and conditions enabling or restricting convection in the melt. The relevant phase diagram provides a prediction of newly appearing phases. During the reactive diffusion, due to the rate of the solid phase dissolution in the melt, conditions of the equilibrium state do not have to be always met because of non-stationary processes [1, 2]. During the diffusion of atoms from the melt B into the solid phase A new phases are formed and they grow, i.e. the diffusion processes take place in the areas with moving interface boundaries. When new phases appear in the course of reactive diffusion, surface and subsurface layers of material of various compositions, properties and thickness are also being formed.

### THEORY

Let us consider a planar interface between the solid phase A and the melt B at the time  $t = 0$ . During dissolu-

tion of the solid phase into the melt the interface solid - liquid moves with the time. The rate of this interface movement is usually considerably greater than the growth of newly nucleating phases with B atoms in the solid metal A. At the interface a diffusion layer will form in the melt, the thickness of which depends on the size of convection in the melt.

For the planar interface boundary when the interface shift during the dissolution is perpendicular to the interface, the relation was obtained [1, 2]

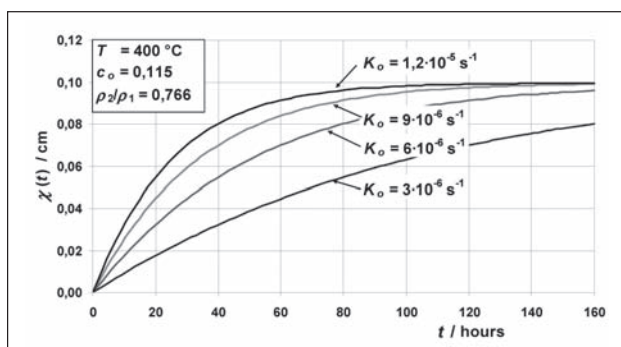
$$\chi(t) = \frac{\rho_2}{\rho_1} \frac{1 - e^{-K_o t}}{\frac{1 - c_o}{c_o} + e^{-K_o t}} l_o, \quad (1)$$

where  $l_o$  is the width of the melt column at the time  $t = 0$ ,  $\rho_2$ ,  $\rho_1$  are densities of the solid and liquid phases,  $\chi(t)$  is the shift of the interface boundary during dissolution,  $K_o$  is the rate constant of dissolution and  $c_o$  is the saturated concentration of the metal A in the melt B. The following equation [2] holds for the time dependence  $c(t)$  of the metal A in the melt

$$c(t) = \frac{\chi(t)}{a + \chi(t)}, \quad a = \rho_2 l_o / \rho_1 \quad (2)$$

Relation (1) describes the time dependence of planar dissolution. Neither the diffusion of atoms B from the melt into solid phase A nor the volume changes during dissolution were taken into account in the model. Convection in the melt will influence the rate of dissolution and therefore the exact value  $K_o$  will partly depend on the geometry, in which the planar dissolution takes place. The relation (1) may be used for an approximate evaluation of the rate constant of dissolution  $K_o$  under precisely defined experimental conditions. Figure 1 illustrates the calculated dependences  $\chi(t)$  for the Cu – Sn system.

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**Figure 1** Graph of functions  $\chi(t)$  – eq. (1) for the liquid temperature of 400 °C in Cu–Sn system and various values of  $K_o = (0,3 \div 1,2) \cdot 10^{-5} \text{ s}^{-1}$  for planar dissolution

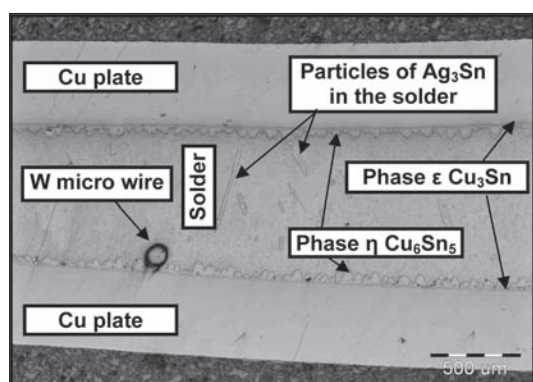
The values of density ratios  $\rho_2/\rho_1 \approx 0,766$  for  $T = 400$  °C,  $c_o = 0,115$  (from the phase diagram Cu–Sn [3]),  $l_o = 1$  cm at  $K_o = (0,3 \div 1,2) \cdot 10^{-5} \text{ s}^{-1}$  were used in the calculations. Time dependences of the component A concentration in the melt, assuming perfect melt homogenisation, are obtained from the relations (1) and (2)

$$c_A(t) = c_o(1 - e^{-K_o t}). \quad (3)$$

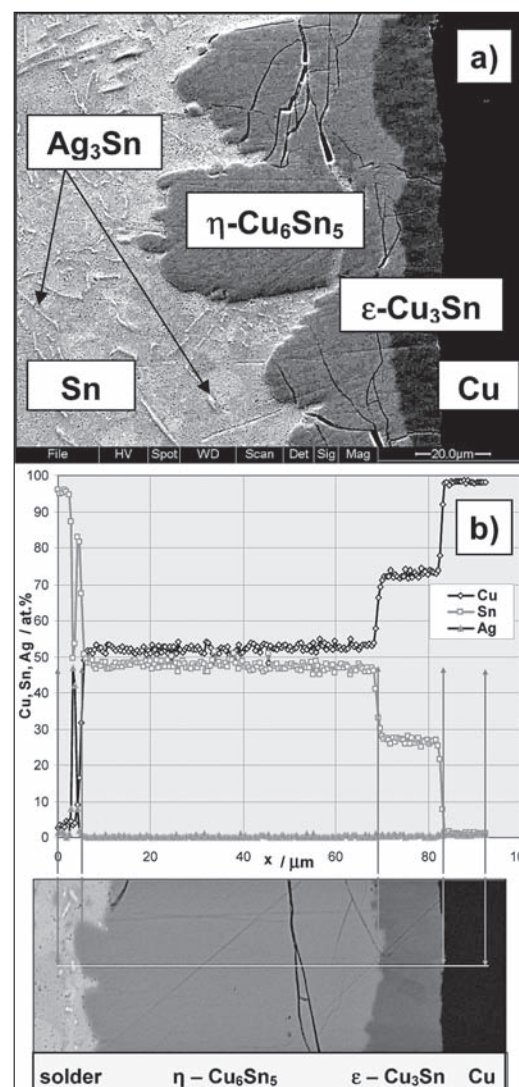
## EXPERIMENTS

The uni-directional experiment was realized using the “sandwich” specimens. A layer of a tin-based solder was inserted between two Cu plates. Five compositions of lead-free solder alloys were used: pure Sn, alloys Sn97Cu3, Sn95,5Ag3,8Cu0,7, Sn95Sb5 and Sn91Zn9. Two plates of high-purity copper were 0,5 mm thick, the other dimensions were 20 x 10 mm. The Sn-based solders inserted between the two Cu plates were rolled down to the thickness of 0,6 mm. Copper plates were covered by a layer of suitable flux. The soldered joint was created using a heating element. The sandwiches were held at the temperature of  $255 \div 285$  °C (above liquid) for the time  $40 \div 120$  s. The prepared specimens were subsequently annealed in the evacuated ampoules at 300 °C for 18, 24, 48 and 92 h – see Figure 2.

The  $\eta\text{-Cu}_6\text{Sn}_5$  grows during annealing at the temperature 300 °C on the interface with the Cu. Copper dissolves in liquid Sn-based solder up to the saturation concentration of approx. 4 at.% (2,2 wt.%) Cu. As a



**Figure 2** Scheme of the soldering experiment and description of the found intermetallic phases after long-time annealing



**Figure 3** Microstructure a) and concentration profiles b) of the joint Cu/SnAg3,8Cu0,7 annealed at the temperature 300 °C for 24 hours

consequence of Sn diffusion into solid Cu, the phase  $\eta$  grows with time and subsequently the phase  $\epsilon$  ( $\text{Cu}_3\text{Sn}$ , 75 at.% Cu and 25 at.% Sn) appears to be close to the pure Cu. The specimens were cooled on the air after annealing and the temperature decreased relatively quickly below the eutectic temperature of 227 °C. The joint copper / solder Sn95,5Ag3,8Cu0,7 is shown in Figure 3 after 24 hours of annealing as an example.

## RESULTS

The growth of the phase  $\epsilon$  should proceed with time according to the parabolic law  $\chi_\epsilon(t) = \alpha \sqrt{t}$  where  $\chi_\epsilon(t)$  is the thickness of phase  $\epsilon$  and  $\alpha$  is the constant, which characterizes the rate of the phase growth. The values  $\chi_\epsilon(t)$  can be obtained experimentally using the metallographic images from relatively large areas or from the X-ray EDX microanalysis. The evaluated values  $\alpha$  from the metallography are presented in Table 1.

The tentative calculations of Sn diffusivities in copper at 300 °C based on the growth of the phase  $\epsilon$  into Cu were performed using the Wagner relation [4-7]:

Table 1 Evaluation of the rate of growth of the phase  $\varepsilon$  in „sandwich“ specimens at the temperature of 300 °C

Difusion joint	t /h	$\alpha \cdot 10^6$ /cm s <sup>-1/2</sup>	mean $\alpha \cdot 10^6$ /cm s <sup>-1/2</sup>
Cu/Sn	18	5,84	5,57
	24	5,10	
	48	4,38	
	92	6,95	
Cu/Sn97Cu3	18	6,50	5,41
	24	6,23	
	48	4,0	
	92	4,92	
Cu/Sn95,5Ag3,8Cu0,7	18	6,6	4,27
	24	3,63	
	48	2,40	
	92	4,46	

$$c_B(x,t) = A \operatorname{erfc} \left( \frac{x}{2\sqrt{D_B t}} \right), \quad (4)$$

where  $B$  is concentration of Sn in (Cu) and  $A$  is concentration of Sn in the phase  $\varepsilon$  (Cu<sub>3</sub>Sn).

Based on the X-ray analysis of concentration curves we searched for the size of the interval  $\Delta x = 2 \mu\text{m}$ , where the Sn concentration in Cu decreased nearly to zero. We can estimate the diffusivity  $D$  from the value  $\Delta x$  and the known time of annealing  $t$  using the equation:

$$\frac{\Delta x}{2\sqrt{D t}} \approx 1,5; \quad \operatorname{erfc}(1,5) = 0,034. \quad (5)$$

Joint	t /h	T /°C	$\Delta x / \mu\text{m}$	$D / \text{cm}^2 \text{s}^{-1}$
Cu/Sn	48	300	2	$\approx 2,6 \cdot 10^{-14}$
Cu/Sn97Cu3	24	300	2	$\approx 5,1 \cdot 10^{-14}$
Cu/Sn91Zn9	92	300	2	$\approx 1,3 \cdot 10^{-14}$

## DISCUSSION AND CONCLUSIONS

In this paper the problems of reactive diffusion at the contact of the solid phase with the solder melt were outlined briefly. Examples of particular experimental arrangements were presented. The main intention was to calculate duration of dissolution of the solid phase for the case of planar geometry. The calculations were performed using the equations (1) and (3) describing the kinetics of dissolution. The aim was to determine the rate constant of dissolution  $K_o$  from experimental results.

When observing the growth of phases on planar interface in the Cu–Sn system for the temperature of 300 °C, very irregular growth of the phase  $\eta$ , especially into the melt, was discovered and estimates of the rate of growth of the phase  $\varepsilon$  into Cu according to the parabolic law were performed, as well for other lead-free solders.

A fast growth of the phases in metal A after long-term heating and detection of the thickness of layers of these phases, i.e.  $\chi_\varepsilon(t)$ ,  $\chi_\eta(t)$  pose considerable time demands on structural and chemical micro-heterogeneity of specimens.

The problems of reactive diffusion were studied for dissolution of copper in melts of various solder alloys

both theoretically and experimentally. We used pure Sn and Sn-Cu, Sn-Ag-Cu, Sn-Sb, Sn-Zn alloys as solder materials. Experiments aimed at the study of a Cu plate dissolution in the solder melt were carried out at various selected temperatures and times. Problems, that have to be solved preferably, were emphasized. Concentration profiles of elements and thickness of layers of phases formed in specimens were determined before and after their diffusion heating by SEM and X-ray microanalyses (WDX, EDX). A great set of data obtained will allow us to derive relationships between the rate of dissolution of the solid phase, i.e. displacement of the interphase boundary  $\chi(t)$  in the melt, and growth rates of intermetallic phases in metal A. The tentative calculations of Sn diffusivities in copper at 300 °C based on the growth of the phase  $\varepsilon$  into (Cu) were performed.

The dissolving rate constant  $K_o$  is a fundamental parameter characterizing the rate of dissolution for the certain configuration of experiment.

The reactive diffusion studied makes it possible to create surface and subsurface layers of controlled thickness in metallic materials.

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**Note:** The responsible translator of English language is B. Škandera, Informetal, Dobrá, Czech Republic